PART ONE
STEREOISOMERS DUE TO RESTRICTED ROTATION IN SUBSTITUTED TRIAMINOMESITYLENES

PART TWO
POLYMERS DERIVED FROM α-ACETAMIDOACRYLIC ACID

BY

BRUCE EMERSON ENGLUND

B.A., Carleton College, 1947
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE COLLEGE OF THE
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URBANA, ILLINOIS

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PART ONE

STEREOISOMERS DUE TO RESTRICTED ROTATION IN SUBSTITUTED TRIAMINOMESITYLENES

Introduction

Stereoisomerism due to restricted rotation about carbon-nitrogen bonds in N,N′-dialkyl-diarylsulfonamidomesitylenes has been studied by Adams and coworkers (1,2). These compounds were found to exist in *cis* and *trans* configurations. The present work is a similar investigation of stereoisomerism of N,N′,N″-trialkyl-tribenzenesulfonamidomesitylenes.

Discussion of Results

Tribenzenesulfonamidomesitylene, prepared by the action of benzenesulfonyl chloride on triaminomesitylene in pyridine solution, was alkylated in aqueous alkaline solution with methyl iodide, ethyl iodide, and benzyl chloride to give the corresponding N,N′,N″-trialkyl-tribenzenesulfonamidomesitylenes. *Cis* and *trans* isomers of each compound were formed and separated by fractional crystallization. When tribenzenesulfonamidomesitylene was alkylated in anhydrous acetone-ethanol solution with ethyl bromoacetate in the presence of sodium hydride, two isomers of N,N′,N″-tricarbethoxymethyltribenzenesulfonamidomesitylene were obtained. Each of these esters was hydrolyzed to a single acid, the acids so obtained being isomeric.

Thermal isomerizations, which suggest that the low-melting isomer of each compound prepared is that of the *cis*-configuration, were readily effected. When the low-melting forms of N,N′,N″-trimethyl-, N,N′,N″-triethyl, and N,N′,N″-tricarbethoxymethyltribenzenesulfonamidomesitylene were heated above their melting points, each was converted to the corresponding high-melting isomer. Decomposition prevented successful isomerization of the tribenzyl and tricarboxymethyl

analogs.

Four additional derivatives of triaminomesitylene were prepared and characterized. They are N-benzenesulfonyltriaminomesitylene, N,N′-dibenzenesulfonyltriaminomesitylene, hexabenzenesulfonyltriaminomesitylene, and triacetamidomesitylene.

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PART TWO

POLYMERS DERIVED FROM α-ACETAMIDOACRYLIC ACID

Introduction

α-Acetamidoacrylic acid, since first reported by Bergmann and Grafe (1), has not been extensively investigated. It has served as an intermediate in the synthesis of cysteines (2) and of leucenol (3). Johnson (4) reported the production of a polymer of α-acetamidoacrylic acid. The purpose of this investigation was to determine the value of α-acetamidoacrylic acid and its methyl ester as acceptors in the Michael reaction, and as monomers for the preparation of polymeric and copolymeric substances.

Discussion of Results

Several attempts were made to add nitromethane to α-acetamidoacrylic acid under a variety of conditions and in the presence of several catalysts. No addition products were obtained. This failure may be ascribed to the low reactivity of α,β-unsaturated acids in the Michael reaction and to the ease with which α-acetamidoacrylic acid undergoes hydrolytic

decomposition.

Methyl α-acetamidoacrylate was prepared by the action of methyl iodide on the silver salt of the acid. It did not readily add indole, piperidine, or ethyl malonate. Extensive investigations to determine suitable conditions for Michael additions to this ester were not carried out.

α-Acetamidoacrylic acid was readily polymerized by the use of 2,2′-bis-azo-isobutyronitrile as catalyst in ethanol solution. The polymer was very similar to that reported by Johnson (4). A catalyst system of ammonium persulfate-sodium metabisulfite-cupric sulfate afforded no polymer in aqueous or ethanolic solution.

Polymethyl α-acetamidoacrylate was first obtained by spontaneous polymerization when the ester was prepared in the absence of inhibitors. It was also obtained by polymerization in benzene solution with benzoyl peroxide or 2,2′-bis-azo-isobutyronitrile as catalyst. When this polymer was formed in, or reprecipitated from solvents containing water, it was a stable hydrate containing one-half molecule of water per monomer unit. The anhydrous polyester softens above 135° C. and is a clear liquid at 210° C., whereas the hydrated form is infusible, decomposing when heated above 300° C.

Copolymers of α-acetamidoacrylic acid and acrylonitrile were obtained by benzoyl peroxide catalysis in ethanol solution and by ammonium persulfate-sodium metabisulfite or 2,2′-bis-azo-iso-butyronitrile catalysis in water solution. The highest molecular weight copolymer contained 95% acrylonitrile and 5% α-acetamidoacrylic acid and was obtained by persulfate catalysis. It had an intrinsic viscosity of 2.92 and was very insoluble except in dimethylformamide. It was infusible, decomposing when heated above 300° C. When a dimethylformamide solution was extruded into water a fiber was formed which, when dried, was relatively strong. When a dimethylformamide solution was spread out on a glass plate and allowed to dry, a clear, colorless, pliable film resulted.

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VITA

The author was born in Minneapolis, Minnesota, on June 16, 1924. He attended the public schools of Winona, Minnesota, and was graduated from Winona Senior High School in June, 1941. He attended Carleton College, Northfield, Minnesota, from September, 1941, to June, 1943, and the following month entered active duty with the United States Naval Reserve. He was released to inactive duty July, 1946, and returned to Carleton College in September of that year. He was awarded the degree of Bachelor of Arts in February, 1947, and at that time entered the Graduate College of the University of Illinois. He held teaching assistantships from February, 1947, to August, 1948, and was awarded the degree of Master of Science in February, 1948. He held the Standard Oil Company of Indiana Fellowship during the year 1948-1949, and has been an Atomic Energy Commission Pre-doctoral Fellow since July, 1949.

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